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US ARMY  
LABORATORY COMMAND  
MATERIALS TECHNOLOGY LABORATORY

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## SELF-PROPAGATING REACTIONS FOR SYNTHESIS OF HIGH TEMPERATURE MATERIALS

April 1991

MICHAEL A. RILEY, PETER D. ZAVITSANOS & JOSEPH J. GEBHARDT

General Sciences, Incorporated  
205 Schoolhouse Road  
Souderton, PA 18964

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FINAL REPORT

Contract DAAL04-87-C-0083

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U.S. ARMY MATERIALS TECHNOLOGY LABORATORY  
Watertown, Massachusetts 02172-0001

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U.S. Army Materials Technology Laboratory  
Attn: SLMCT-PR1  
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Key Words

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Boron Powders  
Titanium Diboride  
Heat of Reaction  
Exothermic Reactions  
Density

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## ABSTRACT

The goals of this effort are focussed on low cost processing technology for the production of high density, high purity, monolithic ceramic (titanium diboride) plates. The investigator's approach centered on the Self-Propagating High-Temperature Synthesis (SHS) technique for forming high purity ceramics. This technique involved the blending of high purity elemental powders of titanium and boron to stoichiometric balance, pressing the powders into a rigid body and heating the body to a reaction temperature in the range of 700 - 1000°C. At the reaction ignition temperature, the elemental constituents would exothermically convert to crystalline titanium diboride while producing large amounts of energy (1.2 kcal) and temperatures in excess of 3000°C. This process was combined with simultaneous compressive forces delivered by high strength springs. The application of pressure at the precise instant of reaction produced highly ductile/semi-solid ceramic structure amenable to low pressure densification.

Process parameters examined in this program included pressure range requirements, unreacted "green body" density effects, metallic "sintering aid" additives and intermediate exothermic reaction phase additions such as Ni Al, Ni Ti and Ti Al.

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## INTRODUCTION

Hard ceramics including  $\text{TiB}_2$ , produced by conventional methods such as sintering and hot pressing require expensive high temperature process steps and machining which add significant cost to the material. The use of exothermic, self-propagating reactions (SHS), have recently received interest especially by the Soviets to form high purity refractory compounds especially in the boride and carbide systems. The cost effective production of abrasive compounds, cutting tools and high hardness monolithic, refractory materials has been claimed.

The SHS process, at its basic level, involves the intimate blending of elemental powders at stoichiometric levels (in this case titanium and boron). Once blended, the materials are pressed into monolithic shapes and heated at one point to a reaction temperature (700 - 1200°C). Upon achieving the reaction temperature, the remaining body is transformed via self-propagating thermal wave into intermetallic or ceramic body based upon the original binary mixture ( $\text{Ti} + 2\text{B} \rightarrow \text{TiB}_2$ ). a schematic of this process is shown in Figure 1.

Most of the advantages of the SHS process have been discussed by the Soviets as well as by the U.S. community and center on the following:

1. No significant process heat necessary.
2. Material can be shaped during the reaction and, therefore, requires minimum machining costs.
3. The temperature generated during the reaction ( $\sim 3500^\circ\text{K}$  as measured by radiometer in this laboratory) is higher than conventional techniques, and can thus, in principle, provide higher purity compounds.
4. The higher process temperature and melting in some cases, can favorably influence microstructure and other significant properties.

Lightweight ceramics which can be prepared by SHS reactions are being considered as candidates for armor. Limited testing to date has identified the generic properties which can maximize armor performance. They are as follows:

1. Highest Chemical Purity
2. High Microhardness
3. High Young's Modulus
4. High Weibull Modulus (High Fracture Toughness)
5. Grain size less than 20 microns

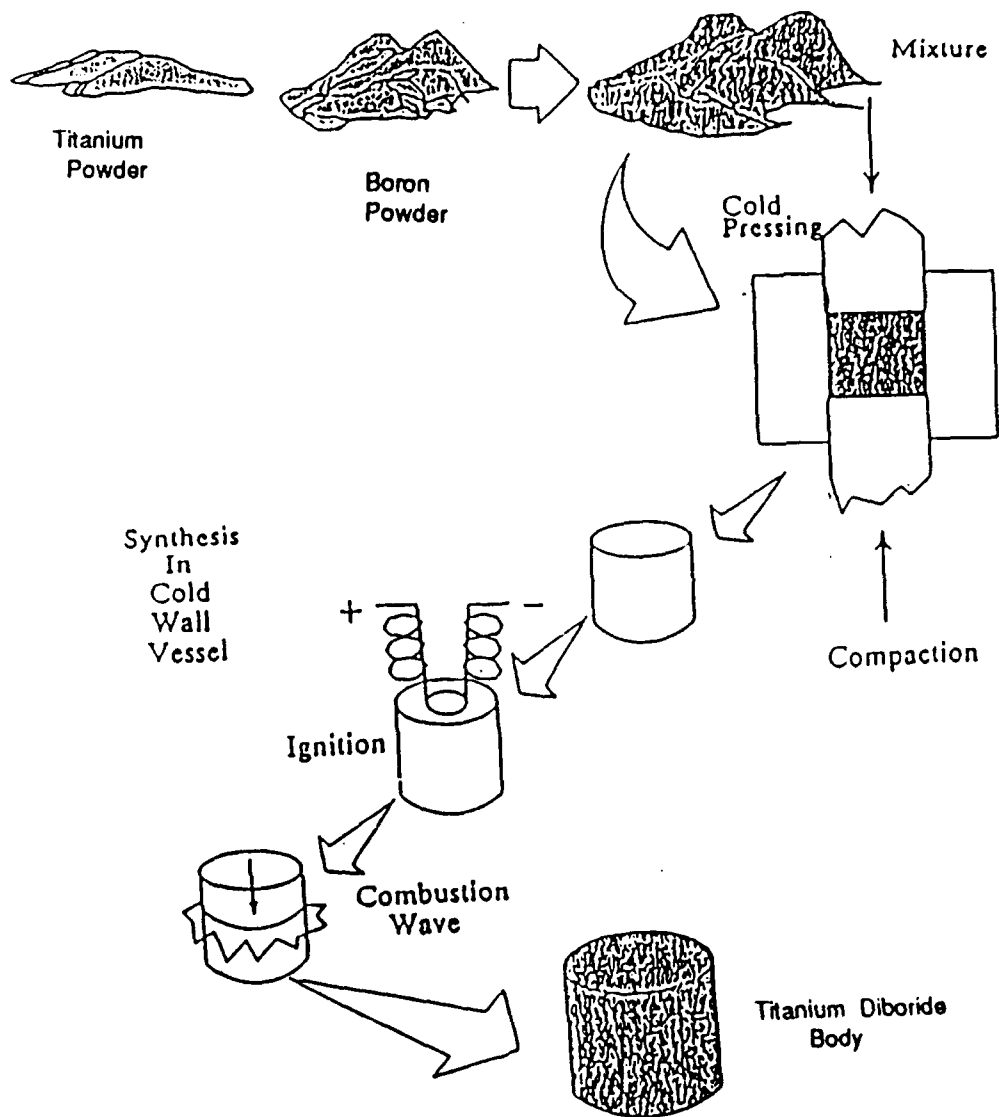


FIGURE 1. Synthesis process for titanium diboride. Powders of titanium and boron are blended to proper stoichiometry, pressed into a green body and reacted with a point source. This ignition causes a self-propagating thermal wave to pass through the body and convert it into titanium diboride.

6. Low Poisson's Ratio
7. Flexure Strength (does not correlate)

In the early 80's, Zavitsanos<sup>(1)</sup> and his group were the first U.S. Scientists to synthesize high density TiB<sub>2</sub> in relatively massive form using the self-propagating high temperature synthesis (SHS) by providing heat externally only for initiation of Ti/2B mixtures, and applying pressure simultaneously. The density was 97% of theoretical and the hardness exceeded that of commercially available hot pressed samples.

The work was continued with ARMY/MTL funds and a more comprehensive study was carried out on synthesis parameters and material characterization<sup>(2)</sup>.

The results of the reaction thermochemistry reported<sup>(1,2)</sup> indicate that the calculated adiabatic temperature of 3600<sup>0</sup>K, obtained in the reaction



exceeds the melting point of TiB<sub>2</sub>, reported as around 3200<sup>0</sup>-K<sup>(3)</sup>. Studies of the microstructure of the reaction pressings confirmed that a liquid phase is present during the process, and the reaction is in a liquid + TiB<sub>2</sub> phase field. Electron microprobe results confirm that liquid phases must be present and secondary phases (possibly TiB and Ti) and contaminants (Si, Fe), are rejected from the liquid as the mass cools and are located at pore surfaces as inclusion in the TiB<sub>2</sub> matrix.

Stoichiometric and excess Ti powder mixes react to form TiB<sub>2</sub> with total metal impurities 0.57 to 0.75%. The formation of a liquid during the reactions is a desirable situation and rapid densification is readily accomplished.

Reaction pressing in graphite dies was used to form a finished sample 1.75" in diameter by at least 1/8" thick. The graphite die assembly with a carbon-carbon filament wound "strongback" retaining ring contained the compact during processing in a furnace atmosphere of flowing N<sub>2</sub> or argon and with an applied force of 15,000 pounds. Figure 2 shows a typical temperature-pressure-time profile used to synthesize and densify TiB<sub>2</sub> from the elemental powder mixtures.

Properties of the TiB<sub>2</sub> obtained during these studies are listed in Table 1 and were sufficiently encouraging to exploit the possibility of utilizing the heat of reaction alone for densification and development of desirable structural properties. This would avoid the requirement of extensive furnace investment, associated energy expenditure and long processing times and enable a relatively low cost, big throughput fabrication process to be developed for TiB<sub>2</sub> tiles of useful size. The work described in this report is directed toward that end.

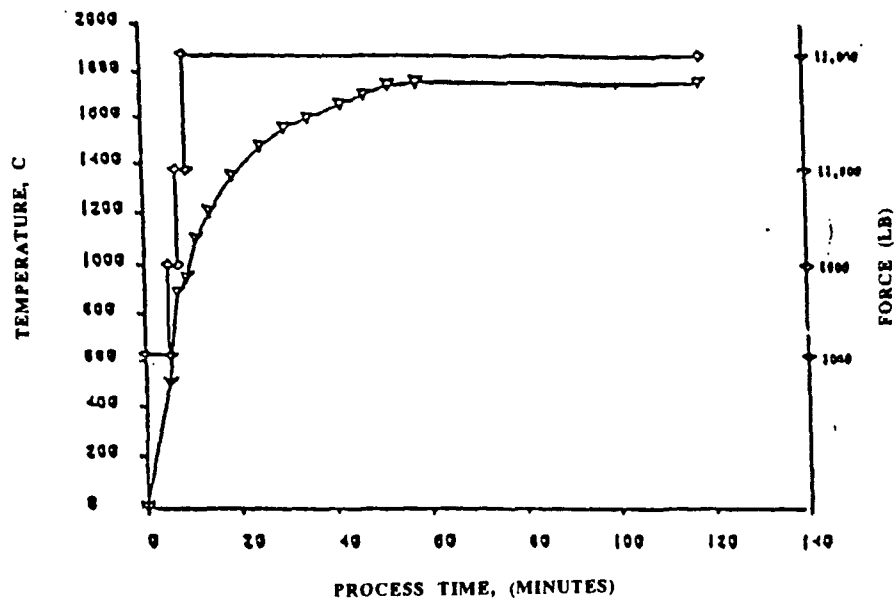


FIGURE 2. Temperature pressure - time profile  
(Zavitsanos & D'Andrea, AMMRC-TR-85-15, June 1985)

**TABLE 1**  
**COMPARISON OF TiB<sub>2</sub> PRODUCED BY THE SHS-PROCESS**

<u>PROPERTY</u>	<u>TiB<sub>2</sub>-HOT PRESSED</u>	<u>TiB<sub>2</sub>-SHS (Ref. 2)</u>
(1) Chemical Purity	98.5%	99.5%
(2) Microhardness (Knoop, 500g)	2345	2200-2800
(3) Young's Modulus (10 <sup>6</sup> psi)	60	(40-80)
(4) Weibull Modulus	28.7	58-85
(5) Grain Size		<20μm
(6) Density	98.5%	97%
(7) Poisson's Ratio	0.11	0.07

Due to the budgetary constraints which forced a premature end to the contract, the goals set forth in the contract tasks have not been achieved. This report describes the results up to the time of the program termination.

## **STATEMENT OF WORK**

The specific contract tasks as determined by the Army are detailed below:

### **Phase I Process Development**

- C-2.1.1 The contractor shall utilize the SHS technique to produce dense titanium diboride wafer (at least 3" diameter x 0.30" thick) for the purpose of optimizing the process to attain physical properties exceeding 90% density, hardness of 2500 kg/mm<sup>2</sup> and three point bend strength of 80,000 psi. The hardness and bend strength values shall not be less than 99% of the stated value.
- C-2.1.2 The contractor shall develop the SHS process to produce rectangular shaped dense titanium diboride tiles having the properties stated in C-2.1.1 in a reproducible manner.
- C-2.1.3 The contractor shall produce a sufficient quantity of 3.0" diameter titanium diboride wafers (a minimum of six), using the optimized processing parameters, for the purpose of conducting characterization and physical property measurements.
- C-2.1.4 The contractor shall perform characterization measurements using x-ray diffraction, chemical analysis for metal, carbon and oxygen content, electron micro-probe analysis on selected titanium diboride samples for the purpose of observing and identifying the appearance of various phases and phase distribution.
- C-2.1.5 The contractor shall perform physical property measurements at room temperature to include density, flexure strength, hardness and fracture toughness on selected titanium diboride samples.
  - C-2.1.5.1 The flexure strength shall be measured according to the specifications outlined in MIL-STD-1942 (MR) 21 Nov 83 using a minimum of thirty (30) tests per tile and four (4) point loading.
  - C-2.1.5.2 The hardness measurements shall be conducted using a diamond pyramid hardness test with minimum of five hundred (500) gram load on a minimum of ten (10) readings per sample.
  - C-2.1.5.3 The fracture toughness shall be determined by using five (5) measurable indents and each of these indents should be greater than five (5) times the grain size.

- C-2.1.6 The contractor shall provide a program review at a site selected by the COR no later than nine (9) months after the start of the contract for the purpose of demonstrating the successful fabrication of titanium diboride tiles conforming to C-2.1.1 and to outline in detail the approach for Phase II before proceeding into Phase II of this contract.
- C-2.1.7 Funds shall not be expended or charges incurred for work under Phase II and III requirements until authorization for such work is approved in writing by the Contracting Officer.
- C-2.2 Phase II Manufacturing of 4" x 4" x 1" Titanium Diboride Tiles.
- C-2.2.1 The contractor shall produce a minimum of three (3) titanium diboride tiles having a minimum size of 4" x 4" x 1" thick using the optimum processing parameters and scale-up development procedures obtained in C-2.1 with a goal of achieving 98% theoretical density.
- C-2.2.2 The contractor shall conduct characterization and physical property measurements as described in C-2.1.4 and C-2.1.5. on each tile produced for C-2.2.1.
- C-2.2.3 The contractor shall evaluate the SHS scale-up process parameters to determine if it is feasible to produce dense titanium diboride tiles larger than 4" x 4" x 1" having the physical properties as specified in C-2.1 with 98% theoretical density.
- C-2.2.4 The contractor shall provide program review at the contractor's site no later than fifteen (15) months after the start of the contract for the purpose of presenting the scale-up technology used to fabricate the 4" x 4" x 1" tiles including all characterization and physical property measurements and to outline in detail the approach for Phase III.
- C-2.2.5 The material from the above program review will be used to determine if the contractor should proceed into Phase III. The determination of the continuance of work shall be the sole responsibility of the Government and if feasibility is not demonstrated to the satisfaction of the COR for any reason, the contract shall be deemed complete at the conclusion of Phase II requirements and the final report shall be required in accordance with DD Form 1423.
- C-2.2.6 Funds shall not be expended or charges incurred for work under Phase III requirements until authorization for such work is approved in writing by the Contracting Officer.
- C-2.3.1 Phase III Production of 6" x 6" x 1" Titanium Diboride Tiles.
- C-2.3.2 The contractor shall produce a minimum of nine (9) each 6" x 6" x 1" titanium diboride tiles with densities approaching 98% of theoretical density using the scale-up facility and the optimized processing parameters established in C-2.2.

- C-3.2 The contractor shall select three (3) tiles from the nine (9) tiles produced in C-2.3.1, subject to the approval of COR, for the purpose of conducting characterization and physical property measurements.
- C-2.3.3 The contractor shall perform characterization analyses as specified in C-2.1.4 on each of the three (3) test tiles selected in C-2.3.2.
- C-2.3.4 The contractor shall perform physical property measurements at room temperature to include density, flexure strength, hardness, elastic modulus, Poisson's ratio and a fracture toughness on each of the three(3) titanium diboride test tiles from C-2.3.2.
  - C-2.3.4.1 Bulk density measurements shall be made on all nine (9) tiles from C-2.3.1. For each of the three tiles selected in C-2.3.2, density measurements shall be made on samples representing nine (9) equal areas of each tile (sample size shall be 2" x 2" x 1").
  - C-2.3.4.2 Flexure strength shall be measured as specified in C-2.5.1.5.1 on a sample population of a minimum of thirty (30) tests per tile.
  - C-2.3.4.3 Hardness measurements shall be conducted according to C-2.1.5.2 on each of the three (3) test tiles.
  - C-2.3.4.4 Elastic modulus measurements shall be made using sonic measuring technique subject to the approval of COR on each of the three (3) test tiles.
  - C-2.3.4.5 Poisson's ratio shall be determined using a sonic measuring technique subject to the approval of the COR on each of the three (3) test tiles.
  - C-2.3.4.6 Fracture toughness measurements shall be conducted according to C-2.1.5.3 on each of the three (3) test tiles.

## **Deliverables**

- C-2.4.1 The contractor shall deliver a minimum of six (6) titanium diboride tiles with a minimum size of 6" x 6" x 1" thick having physical properties as specified in C-2.1.
- C-4.2.2 The contractor shall fully document the SHS procedure used for the scale-up development in producing the titanium diboride tiles from C-2.3.1.
- C-2.4.3 The contractor shall fully document the SHS procedure used for the scale-up development in producing the titanium diboride tiles from C-2.3.1.
- C-2.4.4 The contractor shall prepare a production cost analysis for the SHS method of fabricating 6" x 6" x 1" thick titanium diboride tiles having the physical properties as specified in C-2.1 and to base these figures on production lot of 1,000, 5,000, and 15,000 tiles and include this information in the Final Report.

## EXPERIMENTAL

The SHS process involves a number of process variables that can be influential to a greater or lesser extent in bringing about the desired product requirements. Those variables which have been examined in the program are indicated by an asterisk in Table 2 and are discussed briefly.

## MATERIALS

Materials used in the program include the following:

Titanium Powder (-325 mesh)	AEE
Boron Powder (crystalline) (-325 mesh)	AEE
Boron Powder (amorphous) (2 - 5 $\mu\text{m}$ )	AEE
Boron Powder (submicron)	Callery
Nickel Powder (-325 mesh)	Alfa

The amorphous boron in use has been found to vary in activity in qualitative firing tests and is being monitored by batch number in fabricating SHS-TiB<sub>2</sub> to note inconsistencies.

## STANDARD PROCEDURE

The standard method, used prior to including the variations to be discussed consisted of the following steps:

- (1) Weighing of titanium (-325 mesh) and boron (amorphous) powders in a 1:2 molar stoichiometry with 12% W/O added nickel powder (-325 mesh) for added toughness and improved intergranular bonding.
- (2) Mixing by rolling in air for two hours in a plastic jar with wire screen (1/2" mesh) to break up clumps and aggregates.
- (3) Compressing the mixed powders in a 3" diameter steel mold with steel pistons to a predetermined pressure. (See Figures 3 thru 5).
- (4) Installing the ignition wire (pyrofuse) alongside one piston with 5 - 10 gm of a titanium-submicron boron powder initiation charge.
- (5) Recompressing the powders and initiating the reaction.

TABLE 2. PROCESS VARIABLES

**MATERIALS**

SOURCE

- \* PARTICLE SIZE
- \* PARTICLE SIZE DISTRIBUTION
- PURITY
- REPRODUCIBILITY
- \* ADDITIVES (Ni, TiB<sub>2</sub>, B<sub>4</sub>C)

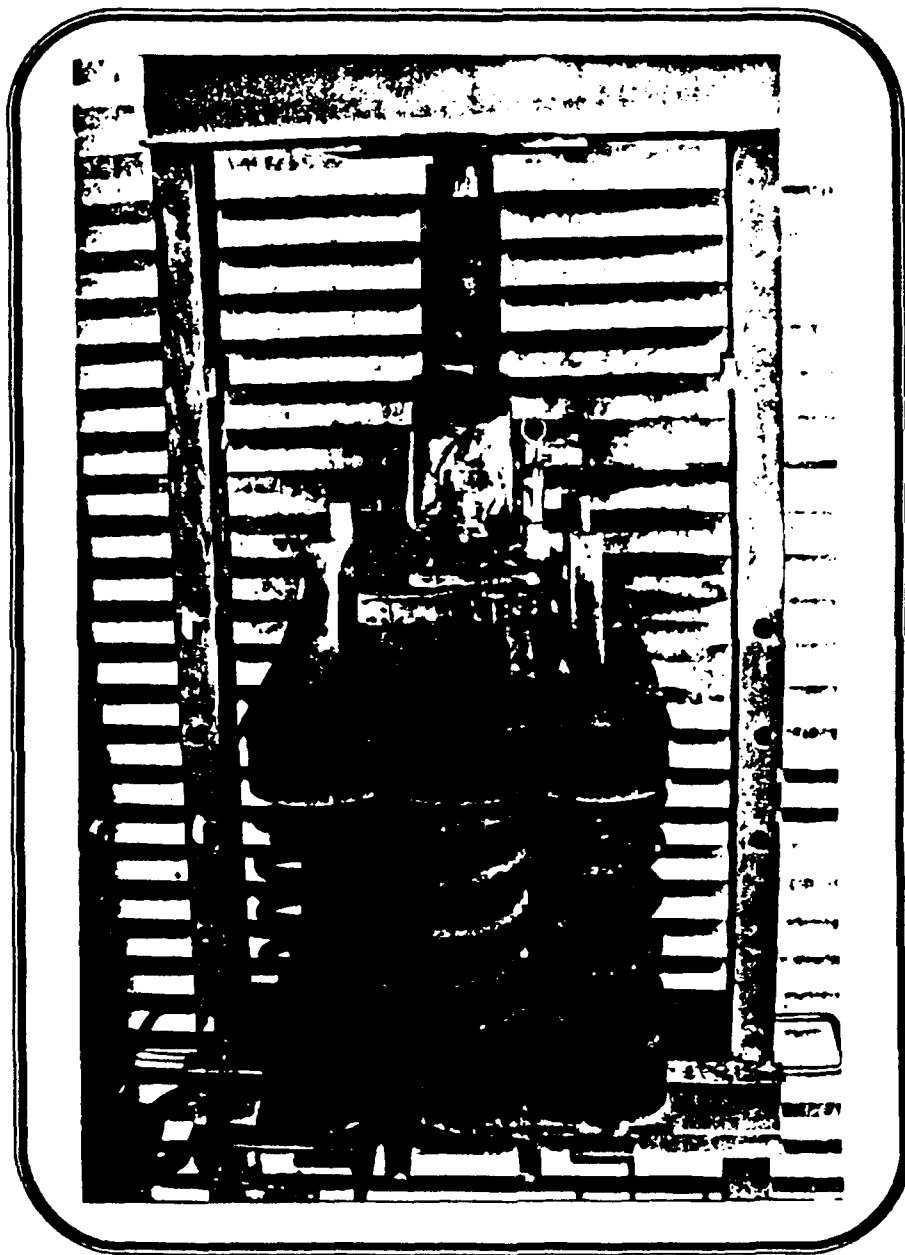
**PROCEDURE**

MIXING - METHOD, TIME, ATMOSPHERE

- \* GREEN CAKE - METHOD, STRENGTH, DENSITY, UNIFORMITY, COMPOSITION
- \* PRE-TREATMENT - TEMPERATURE, TIME, ATMOSPHERE
- DIE DESIGN
- \* CONTAINMENT - DIE CONSTRUCTION
- \* THERMAL CONTROL, INSULATION
- IGNITION
- PRESSURE SYSTEMS
- ALIGNMENT
- \* REACTION TEMPERATURE, TIME
- \* POST TREATMENT

-----

- \* EXAMINED DURING THIS PERIOD



**FIGURE 3.** Low Pressure compaction apparatus. The 3" diameter ram at the top is placed in compression prior to sample reaction. As reacted sample achieves a liquid/ductile state, the spring compresses the ceramic disk.

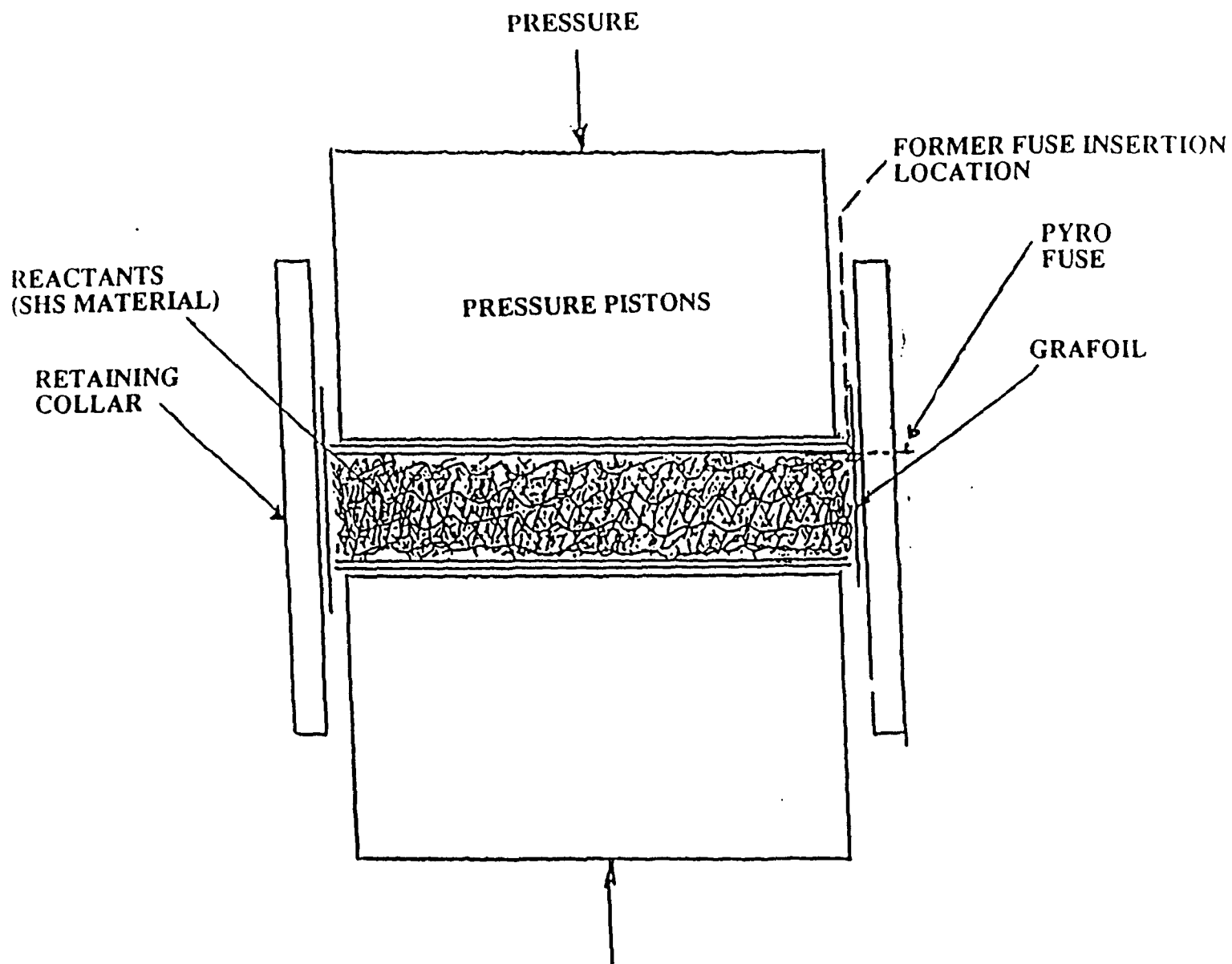
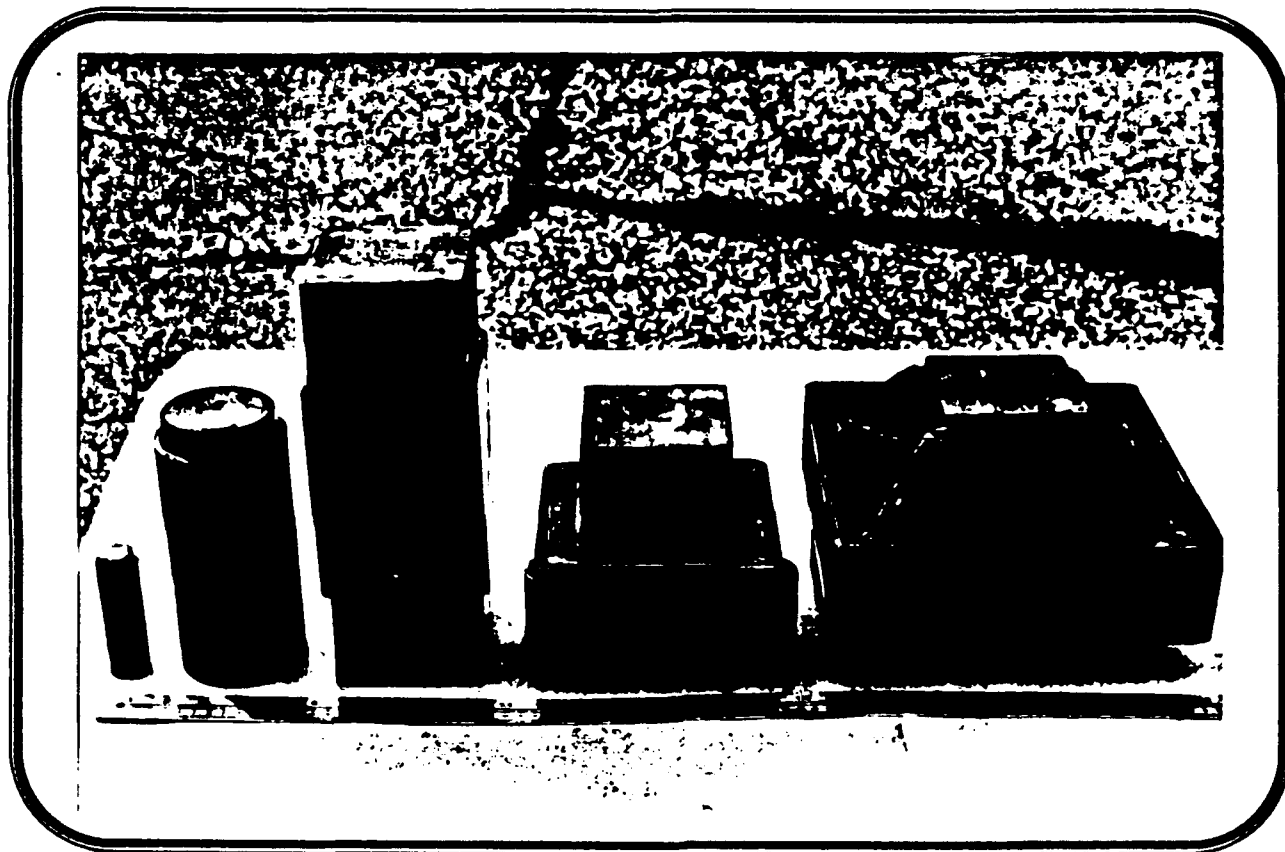
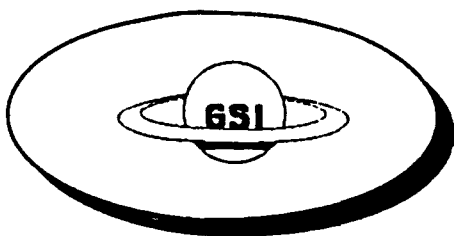


FIGURE 4. Reaction pressing die set-ups used with spring loaded press.



**FIGURE 5.** Compaction dies for in-situ densification process. Sizes ranged from 1" to 3" diameter to 3", 4" and 5".

(4) Installing the ignition wire (pyrofuse) alongside one piston with 5 - 10 gm of a titanium-submicron boron powder initiation charge.

(5) Recompressing the powders and initiating the reaction.

The results of this procedure included the following effects:

(1) Loss of material during reaction - this loss may or may not have been stoichiometric from run to run and may have been a result of expansion of gases in the pockets of approximately 50% dense green cake. Absorbed gases and vapors, especially on the amorphous boron may also have contributed. Loss of material was also increased by the opening alongside the piston left for the fuse wire. Losses between 5 and 40% of the initial weight were noted.

(2) Incomplete reaction of the boron powder which appeared to have been agglomerated into soft inclusions at the periphery of the finished field as well as the top (i.e. away from the initiation side) edges.

(3) Porosity throughout the reaction product, but especially at the edges.

## PROCESS VARIATIONS

Variations made in the standard procedure included the following for the reasons noted:

(1) Introduction of the ignition wire through the side of the mold to reduce clearance of the piston into the mold. In some instances less material was lost, but this approach was not the solution. However, it was incorporated as a standard technique (See Figure 3).

(2) Addition of 15 weight percent excess titanium (i.e.,  $1.15 \text{ Ti} + 2\text{B}$ ) to effect complete reaction. This appeared to alleviate the problem of inclusions of excess boron and was incorporated into the procedure.

(3) Addition of small amount (4 - 5 weight percent) Callery (submicron) boron to increase the heat generated per unit time (faster reaction). This did not appear to improve the effects previously noted.

(4) Use of mixed crystalline (-325 mesh) and amorphous boron in a weight ratio of 38:62. This produced a higher density product (93.3%) on one case and is reserved for future use.

(5) Heat treatment of the mixed powder charge at 900°C, 1500°C in air and under argon at 500°C (2 hrs) prior to loading in the die. A lower loss of powder during reaction was noted in general as well as decreased porosity. This step is now included in the procedure.

(6) Stopping of the ram motion at a point calculated to yield a dense specimen effectively reducing significantly the residual pressure on the final product. Aimed at preventing mechanical failure of the reaction product, it did not appear to solve this problem. Its effect is not yet clear.

(7) Incorporation of selected powdered diluent additives such as boron carbide and prereacted titanium diboride for the purpose of reducing the reaction energy released per unit volume, appeared to reduce density. Metal additives such as nickel and excess titanium were also examined.

(8) Variations in mold design were examined through the use of ceramic and graphite die liners and Fiberfrax external wrappings to retain reaction heat for a longer period to prevent thermal shock from fracturing the product. These were not successful. Carbon felt pads placed above and below the powdered charge caused the pistons to approach each other off-axis, effectively squeezing the molten metal to one side. Alternate approaches are being considered.

Bomb calorimeter measurements of the reaction  $\text{Ti} + 2\text{B} \rightarrow \text{TiB}_2$  have suggested that the reaction is fast enough that sufficient energy is released to raise the adiabatic temperature of the intermetallic compound above its melting point of 3200°K. It is this liquid formation during reaction which allows dense compacts to be made under relatively low pressure. If a liquid-former capable of wetting  $\text{TiB}_2$  is also added, then more liquid phase is present and a longer pressing time results. Nickel has been added by other investigators<sup>(3)</sup> and has also been used at GSI. Pure  $\text{TiB}_2$  compacts have been reaction pressed to greater than 80% of theoretical density under moderate pressures of ~1000 psi. These lower densities are believed to be the result of trapping unreacted islands of titanium and boron within a dense  $\text{TiB}_2$  structure. A suggested mechanism for this observation is that the liquid phase duration is so short that gas pockets can develop around unreacted material and insulate the material from the reaction. However, if a small amount of nickel is added, the liquid phase is sustained over a longer period of time span and gas pockets are collapsed and eliminated. As a result, densities of over 90% of theoretical are readily achieved and in some instances, on one inch diameter samples, full theoretical densities were reached. Knoop hardness measurements of this material were made and values in the area of 1400 were recorded with a 1 kg weight. These values were low when compared to prior work.

## RESULTS

Prior to incorporation of a two hour heat treatment at 500°C in flowing argon, most runs yielded low density, porous products or tiles that were of lower density than would be expected from the quality of powders utilized. This was due to entrapment of absorbed gases and oxides on both the boron and titanium or loss of part of the charge by explosive expulsion of the gas through gaps between the piston and cylinder of the die. After outgassing, loss of material was reduced and densities were usually about 90% of theoretical. In nearly all cases, the tiles were found to have broken into three or more parts; the presence of whiskers and oxidation regions on the fractured surfaces suggests fracture occurred at a temperature high enough for such growths to occur. Stringers or solidified small rivulets of a white glassy material were sometimes seen possibly the result of oxides on the titanium particles.

In several instances, regions of unreacted powder, probably boron, were found at the edges and corners of the tile farthest from the initiating charge. Addition of excess titanium overcame this in some cases, but not universally helpful, suggesting that the balance between the rate of reaction, i.e., heat generation and loss of heat to the mold parts was not optimal. These regions were found to consist largely of boron, identified by interference from the large amorphous shoulder at the low mass end of the EDAX trace, plus magnesium, the major containment in the starting powder, as well as some titanium.

Microstructural examination showed that, despite outgassing and the addition of nickel, significant blowholes were clearly visible while the nickel had segregated to the grain boundaries.

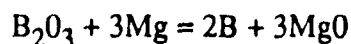
Portions of higher density runs were examined and specimens selected for three point flexural tests. Average values of 346, 170 and 113 MPa from specimens of 98, 88.5 and 85% theoretical density respectively were obtained with a maximum of 423 MPa for a specimen 97.8% dense. These compare well with results obtained in Ref. 2 but show greater scatter so that conditioning or heat treatment will be required after the initial reaction to improve intergranular bonding and uniformity.

Fracture of the reacted tiles appears to be the result of thermal shock in most cases and requires better management of the residual heat of reaction. This is currently being approached through improved mold design and insulation. Too rapid a release of pressure after reaction may also play a part and this being addressed by the use of a more controllable pneumatic system.

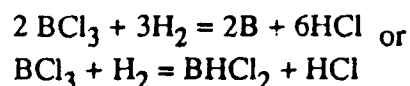
## SHS Reaction/Compaction of $\text{TiB}_2$ : Gas Impurity Effects

This phase of the program examined the role of the starting materials (boron in particular) absorbed impurities and their effects on in-situ densification processing.

The product of commercial elemental boron is accomplished primarily through the thermomagnesium method:



Other methods include the reduction of boron compounds by hydrogen



where the boron bromide is reduced by hydrogen more easily than boron chloride at  $750^\circ - 850^\circ\text{C}$ .

Commercial materials from both processes were obtained for incorporation into the test matrix as was crystalline boron, a more pure but expensive grade of boron. The impurity breakdown of the various materials is shown in Table 3. It is clear that  $\text{O}_2$  and  $\text{Mg/MgO}$  will cause the resultant impurities if not minimized before reaction. It was found that the high purity materials (Vendor A) immediately gained 1 - 3% oxygen upon exposure to air. Their combined higher cost storage difficulties caused them to be least desirable for large scale processing. Based on the prohibitive costs of crystalline boron, the amorphous materials from vendor B were determined to be most adequate for the program goals.

In each case, the rapid formation of the impurities as gases during the SHS thermal pulse resulted in large pore channels forming inside the structure while exiting gases carried away as much as 40% of the resultant  $\text{TiB}_2$ . Examination of the internal structure revealed the following:

1. large areas of discoloration indicative of  $\text{TiO}_2$
2. large channel formation due to gas blow-out
3. strong sulphur-like odor indicative of borane formation

Items 1) and 3) strongly indicate that the  $\text{Ti} + 2\text{B}$  reaction did not go to completion but, rather, large areas of each element were isolated to react with the gas impurities upon quench. This condition was verified by fracturing some green body compacts of  $\text{Ti/B}$  and aluminum. The aluminum serves as a color differentiator and the fracture surfaces shown in large agglomerates of boron powder. This agglomeration ( $100\mu\text{m} - 1\text{mm}$ ) problem was due to moisture pickup by the

**TABLE 3. OXYGEN IMPURITIES IN BORON POWDERS**

		AS RECEIVED	AIR EXPOSED
Boron	Vendor A	1.5-1.8%	1.8-3.0%
	Vendor B	1.6-3.0%	1.9-3.5%
Crystalline	Vendor C	1.0-1.2%	1.0-1.3%

boron powder in storage. This problem can only be truly overcome by complete inert gas and dry box handling during each step of the green body preparation. Due to the potential fire hazard from bake-out of the blended powders, moisture removal can only be done to the individual pre-mixed powders.

While absorbed moisture can be reduced with bake-out at 120<sup>0</sup>C, the titanium powders also contain a monolayer of hydride which is removed at temperatures in excess of 450<sup>0</sup>C. This step is best accomplished in vacuum and has thus far not been attempted since it is both expensive (diffusion pump system) and time consuming (powder quench in vacuum 48 hr. minimum for smaller quantities).

### **Post SHS Reaction Heat Retention**

A leading cause of the specimen fracture evident in all previous efforts is the rapid thermal quench which the materials undergo. This quench takes the ceramic body through rapid tension and compression at temperatures below the ductile-brittle transition temperature, essentially ripping the body apart. An additional difficulty with past samples again involved the rapid quench and its effect on non-uniform material quench. The walls also quench first and the material densifies into concave shape. The shape served to pin down the sample at the edges and assist in material fracture by inhibiting the ceramic's ability to contract.

To overcome these difficulties, the die configuration shown in Figure 6 was developed. Patterned after similar devices used in Soviet SHS research, the device consisted of a massive graphite sleeve (2" thick walls) with close tolerance graphite rams. The SHS precursor material is centered in a fluid die of zircon sand. The sand serves three purposes: 1. thermal barrier, 2. isostatic pressure and 3. impurity effluent gas absorption. Not shown in the diagram is a small quantity of low density Ti/B (1:2) mixture placed around the igniter to assist in the uniform firing of the SHS body. This design exhibits extreme resistance to the thermal cycling it undergoes (thirty test firings without breakage) and also has completely eliminated the undesirable material blowout that always occurred in the metal dies.

While this design is a major improvement in many ways, the Ti/B (1:2) reactions still resist densification and contain internal oxides and boranes. Total body density as high as 80% have been achieved for TiB<sub>2</sub> monoliths without binders. Materials are recovered with no surface cracking but specimens fractured for analysis showed gas channel porosity and internal oxide formation. In comparative studies, the Ti/C SHS system was also reacted/compacted in the same apparatus. Although reacting at a lower temperature, the TiC system achieves densities  $\geq 85\%$  with little if any internal contamination. This difference is based on the processing, the Ti/C

# Die Configuration for In-situ Reaction/Densification

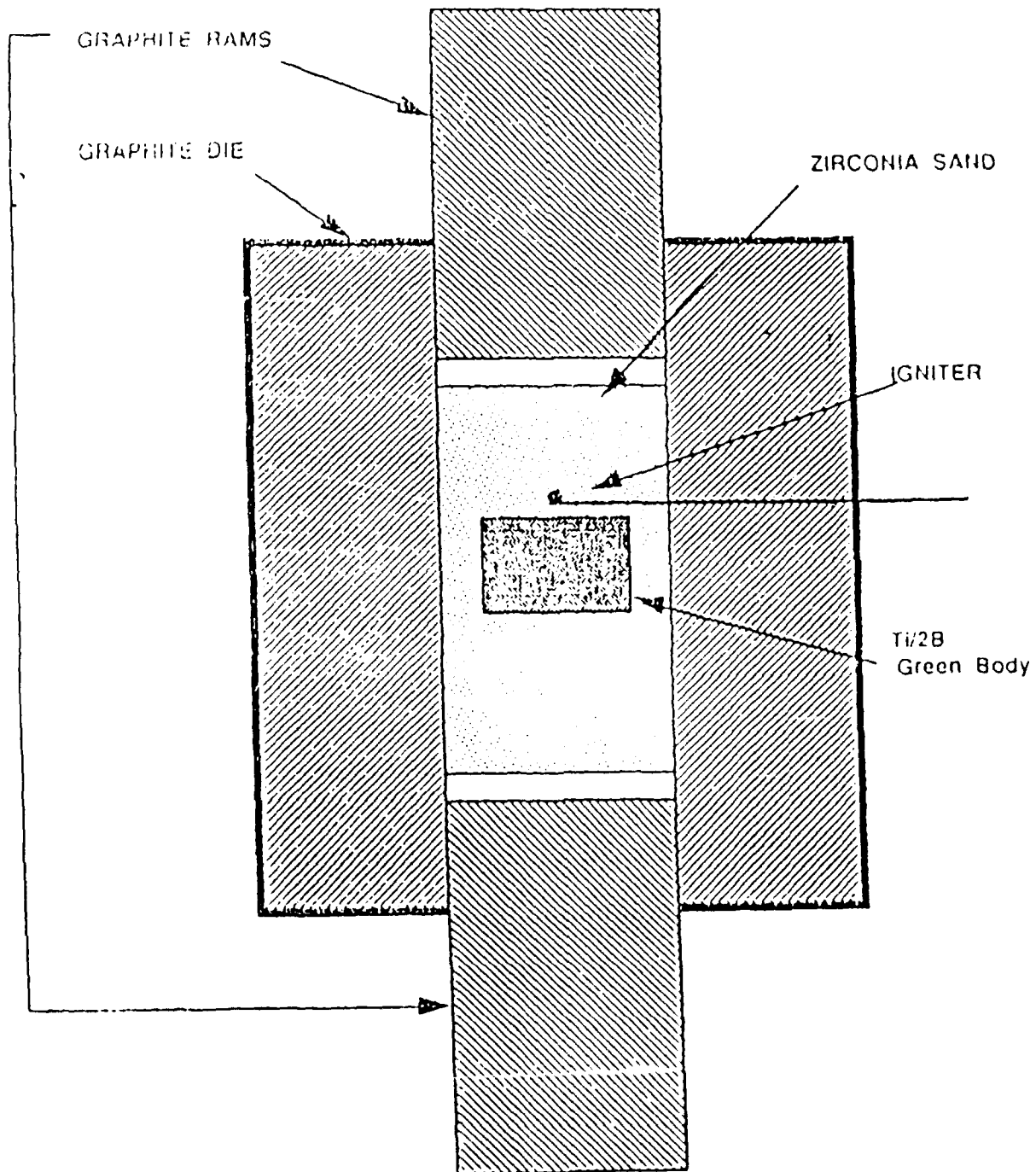


FIGURE 6. Insulated die configuration for in-situ Reaction/Densification

system yields little if any gas and flame during reaction.

### Internal Heating via Secondary SHS Reaction

Due to the limits in the current press and die design, the third effort concentrated on internal heating of the SHS body by incorporating small quantities of a second exothermic reaction. To accomplish this, powders of Ni/Al and Ni/Ti were blended into the Ti/2B system to form an intermetallic grain boundary phase. These intermetallics were chosen due to their delayed reaction mechanism. While their reaction temperature are far lower than the Ti/2B system (1200 - 2000°C vs. 3200°C), their preheat reactions allows the reaction quench curve to be extended for several seconds in the region of the ductile - brittle transition for  $\text{TiB}_2$ . By the uniform dispersion of the Ni/Al and Ni/Ti particles throughout the green body, it is hoped that a very uniform temperature distribution can be achieved.

Results of this approach confirm the ability to apply uniform heat. Rather than the sample forming a concave body as it did in previous tests, the compacts formed with intermetallic phases were uniformly compacted, indicating even heat distribution during compaction.

Table 4 lists the Phase I experiments carried out as well as comments related to the variations just discussed. Portions of certain runs were selected for machining into test bars suitable for three point flexure tests. These results are given in Table 5 and were compared to data obtained previously by Zavitsanos and D'Andrea<sup>(1)</sup>. The same trend is evident in both sets of data, i.e., that flexure strength is related to density. Qualitatively it also appeared in general that the processed discs tended to fail in the die into a number of pieces related to density. The majority, with densities between 80 and 90% of theoretical yielding four quadrant shaped pieces. A few of higher density fragmented more, while low density specimens (particularly those containing unreacted boron carbide) tended to remain unbroken.

Scanning microscopy and probe analysis supported previous results showing nickel to be concentrated at grain boundaries. Circular blowholes were evident indicating formulation of a liquid phase during the reaction, quite possibly the nickel of nickel-titanium phase. Whisker formation and glassy stringers, possibly titanium oxide, were visible at low magnification (40 X) on fracture surfaces.

### DISCUSSION

The experimental variations introduced during this work period appear to have resolved the problem of incomplete reaction (addition of 15 weight percent excess titanium) and alleviated the

TABLE 4  
SHS PRESSINGS 3" DIAMETER DIE

SPECIAL CODE	COMPOSITION	PRESSURE PSI	LOSS (%)	DENSITY (% THEOR)	NO H.T.	COMMENT
080288-1	1.5 Ti + 2B + Ni	991	1	79.8	NO H.T.	P HELD
080388-1	1.5 Ti + 2B + Ni	1487	33	81.9	"	"
080388-2	1.10 Ti + 2B + Ni	1133	-	89	"	"
080488-1	1.10 Ti + 2B + Ni	992	-	90.5	"	"
080488-2	1.10 Ti + 2B + Ni	1487	17	89	"	"
080588-1	Ti + 2B + Ni	1232	29	93	"	"
080588-2	1.15 Ti + 2B + Ni	1232	9	91	"	"
080888-1	1.0 Ti + 2B + Ni	1232	-	94	"	"
080888-2	1.15 Ti + 2B (CR) + Ni	765	-	95	"	"
080988-1	1.10 Ti + 2B + Ni	1232	-	90	"	"
080988-2	1.10 Ti + 2B	1232	17	99	"	"
081088-1	1.10 Ti + 2B	779	33	82.9	"	"
081088-2	1.10 Ti + 2B	1232	13	84.7	"	"
081188-1	1.10 Ti + 2B	unavailable	11	84.6	"	"
081188-2	1.10 Ti + 2B + Ni	"	14	89.3	NO H.T.	PRESS STOPPED
081288-1	1.10 Ti + 2B	"	4	86.2	"	"
081788-1	1.10 Ti + 2B	"	6	84.9	"	"
081888-1	1.10 Ti + 2B	"	41	79.3	"	"
081988-1	1.1 Ti + 2B + 17% B <sub>4</sub> C	"	22	77	1 Hr 150° C	"
082388-1	1.1 Ti + 2B + Ni	"	14	73	"	"
082488-1	1.15 Ti + 2B + Ni	"	35	65	"	"
082488-2	1.1 Ti + 2B (CRY) + Ni	"	9	90.3	2 Hr 150° C	"
082588-1	1.1 Ti + 2B + Ni	"	4	92	"	"

TABLE 4 (CONT'D)  
SHS PRESSINGS 3" DIAMETER DIE

SPECIAL CODE	COMPOSITION	PRESSURE PSI	LOSS (%)	DENSITY (% THEOR)	COMMENT
082688-1	1.1 Ti + 2B (CRY) + Ni	1232	6	66	2 Hr 90° C PRESS STOPPED
082688-2	1.15 Ti + 2B + Ni + 4% Ti/2B (CALL)	"	5	97	NO H.T.
083088-1	1.1 Ti/2B + Ni + 4% Ti/2B (CALL)	1232	10	93.7	24 HR 90° C PRESS STOPPED
090188-2	1.15 Ti/2B + Ni +5% + Ti/2B (CALL)	1232	8	74.8	NO H.T.
090688-1	1.1 Ti/2B + 12% Ni	1232	4	72.3	2 HR 150° C
090788-1	1.1 Ti/2B + Ni	"	2	82.6	2 HR Ar. 500° C
090988-1	1.1 Ti/2B + Ni	"	25	85.1	"
091488-1	1.15 Ti/2B + Ni	1232	7	88.4	"
091988-1	(.38/.62 AMOR/CRYST) 1.15 Ti/2B + Ni	1232	13	93.3	"
100688-1	(.38/.62 AMOR/CRYST) 1.15 Ti/2B + Ni	1232	25	"	2 HR 150° C
100688-2	1.15 Ti/2B + Ni	1232	4	89.5	2 HR 200° C
1012881	1.15 Ti/2B + Ni (METHOCEL BINDER)	1232	36	87.2	2 HR 500° C
102088	1.15 Ti/2B (4 x 4 x 1" PLATE)	1232 750	36	72.7	NO H.T.
102688	1.15 Ti/2B + 6% Ti B <sub>2</sub>	1232	10	74.7	2 HR H.T. 170° C

NOTES:

- 1) ALL BORON IS AEE AMORPHOUS UNLESS OTHERWISE INDICATED
- 2) NI ADDED AS 12% OF TI + B WEIGHT IN ALL CASES
- 3) PRESSURE DEDUCTED FROM FIGURE 2.
- 4) PRESSED STOPPED: STEEL SHIMS INSERTED TO STOP PRESS AT THEORETICAL TILE THICKNESS CALCULATED FROM SPECIMEN WEIGHT.

TABLE 5. Three point flexure test results

TEST	SPECIMEN	DENSITY (% THEOR)	FLEX STRENGTH (MN/M <sup>2</sup> )	(KSI)
1	80888	98.2	270	39.2
2	(1.15 Ti + 2B + 12% Ni)	97.8	423	61.4
3	80488	87.4	149	21.6
4	(1.15 Ti + 2B + 12% Ni)	87.1	164	23.9
5		88.7	149	21.6
6		90.7	216	31.4
7	91988	79.4	106	15.4
8	(1.15 Ti + 2B)	80.7	102	14.8
9	(AMORP + CRYST B)	86.5	96	14
10		85.3	107	15.5
11		86.5	110	16.5
12		87.4	122	17.7
13		89.4	141	20.5
14	91488	86	94	13.7
	1.15 Ti + 2B + 12% Ni (AMORP + CRYST B)			

	SPECIMEN DIMEN.
1 - 6	25 MM X 7.5 MM X 4.66 MM
7 - 14	25 MM X 9.7 MM X 3.21 MM

	STRESSED VOLUME
	885 MM <sup>3</sup> .054 IN <sup>3</sup>
	787 MM <sup>3</sup> .048 IN <sup>3</sup>

problem material loss during reaction to some degree. Fracture of the firing specimen remains a problem and may be related to the manner of pressing, i.e., timing of pressure application and release relative to the reaction propagation and level of pressure applied. Examination of certain specimens showed whiskers and glassy oxide stringers to be present on the fracture surface as well as colored areas suggesting reaction of titanium with oxygen (dark purple) and/or nitrogen (gold). This suggests that fracture as the specimen had occurred at a relatively high temperature, perhaps immediately after solidifying or on solidification temperature. Thus fracture of specimens could be due to mechanical or thermal effects (quenching) or a combination of these factors. Efforts to prevent thermal shock cracking by improved insulation and addition of a lower melting, non-reacting metal (copper) have not been effective thus far.

As noted above, mechanical properties were found to be related to density of the specimen. Specimens with the highest measured strength (see Table 5) had a fine-grained metallic appearance with little or no significant porosity. However, specimens had been cut from as-formed SHS products with no post-formation annealing which might heal microcracks and improve intergranular bonding.

## CONCLUSIONS

Results from this abbreviated effort show that the reaction of titanium and boron to fabricate  $\text{TiB}_2$  monoliths in relatively massive form is potentially feasible. Significant steps are required however, to optimize the process; among the remaining challenges are:

1. Powder Purity Control - The fine powders utilized in the process (-325 mesh Ti and submicron B) naturally possess high quantities of absorbed gases (primarily hydrogen from Ti and  $\text{H}_2\text{O}$  for B). Without careful removal of these impurities, the rapid rate of temperature rise causes extremely high internal gas pressures to occur. This rapid pressure formation causes blowout of contained materials resulting in damage to the green body and the reacted sample. Moreover, the inability to remove all impurities during the reaction results in internal flaws which serve as fracture initiation sites.

The cleaning procedure requires temperatures in excess of  $400^\circ\text{C}$  for hydrogen removal. Due to this relatively high temperature, the powders must be cleaned individually to avoid the possibility of reaction; this step requires powder isolation from atmosphere and each of these steps requires added processing expense.

An alternate approach would be to slowly bake out the pressed green body until it reaches the reaction temperature. Again, the energy requirement for body purification adds to processing cost.

2. **Improved Insulation of Post Reaction Sample** - Immediately after the reaction temperature is reached, the ceramic body undergoes a rapid, non-uniform quench process which induces tensiled compressive modes randomly in the sample. This results in severe micro-cracking. Once again, as an initial temperature ramp provides "gentle" removal of impurities, a final ramping down will gradually receive the internal stresses in the ceramic body and prevent fracture. The systems examined in this program were insufficient and an external heat source is recommended.

A further benefit from such heat control would be improved bonding between grains in the body. The low values for flexure strength obtained in our test specimens is indicative of extremely poor intergranular bonds. While this is due partially to impurities, there is microstructural evidence that poor intergranular bonds existed due to the extremely short sintering period allowed by the reaction.

3. **Enhanced Pressure Delivery** - While the methods for densification were designed with low cost as a primary motivation, the spring assembly was not able to achieve full density ceramic structures. In ceramic samples reacted with no metallic additive, maximum densities were on the order of 95% theoretical. Only when metallic binders or second phase intermetallic reactants were added did densities achieve > 98%. While the other problem areas previously mentioned may play a role in limiting the achievable density, tests with reactions involving less materials with little or no gas causing impurity (titanium + graphite) were also incapable of achieving full density.

An improvement in this area would be to utilize a hydraulic ram capable of higher pressures. Such a system can be remotely operated so that pressure can be maintained before, during and after the SHS process.

While the three main challenge areas add to the complexity of the synthesis/fabrication operation, one or all are necessary to overcome the current technical barriers. While this effort has not shown feasibility for the original low cost processing technique, sufficient information has been gathered for future studies aimed at more realistic processing of SHS reactions requiring more stringent process controls.

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